SSERVI-ESF14-072

Author: JOSHUA CAHILL

POSTER

Geochemistry/Petrology

Determination of synthetic olivine near-infrared optical constants

Mineral optical constants (n, k) are critical for radiative transfer spectral modeling techniques pioneered by Bruce Hapke. Building upon [1, 2], Trang et al. [3] published optical constant regression coefficients for natural and synthetic pyroxenes and natural olivines. The samples used include synthetic pyroxene samples created [4, 5] and natural olivine samples previously characterized by [6-8]. Trang et al. [3]'s analysis suggested the most reliable optical constant measurements were determined using spectra collected by RELAB. This analysis was performed using a combination of MGM and statistical regression analysis techniques. In this way, regression coefficients are determined that allow a computation of optical constants with changing composition using radiative transfer theory. A discovery made during this study was an apparent influence of Mn2+ on absorption strengths of natural olivine spectra [3]. As the abundance of Mn2+ increases and Mg2+ decreases, the compositional relationship between Fe2+-Mg2+ (i.e., Fo-content) becomes a non-linear relationship; the strength of all three of olivine absorptions is curbed when fit, and increases the scatter of k variance with composition. However, neither olivine absorption centers nor widths show any changes in their systematic variation with Fe2+-Mg2+ composition. This discovery was made more prescient recently when [9] effectively constrained optical constants for silicates directly from near-infrared spectra of lunar soils. While this method and optical constants appear to plausibly be more effective, it is unclear exactly how and why lunar mineral optical properties would be so different as to result in significantly underestimating feldspar and overestimating mafic silicates in spectral models of the lunar surface. However, likely influences upon these measurements include trace elements, shock, melting, and devitrification.Here we characterize standard synthetic olivine relative to that of naturally occurring olivine optical constants (i.e., lunar/terrestrial vs. synthetic). We begin by (1) examining synthetic olivine optical properties free of trace element influence and (2) see if we can begin to effectively isolate the influence of Mn2+ on naturally occurring olivine reflectance spectra. The synthetic olivine samples used here were produced by [4, 5] and characterized by [10]. Initial MGM analyses of synthetic olivine appear to be devoid of the absorption strength 'curbing' we observe in the natural olivines for the 0.9, 1.1, and 1.3 _m bands [11]. These synthetic samples are more evenly distributed in terms of the Mg' composition and show less scatter in MGM fitting parameters, especially absorption strength.

SSERVI-ESF14-073

Author: CJ CAREY

Geochemistry/Petrology

ORAL

Machine Learning Tools for Remote-Sensed Spectra from Airless Bodies

Interpretation of remote-sensed spectroscopic data from surfaces of airless bodies relies on a combination of crystal field models and empirical fitting routines to produce estimates of mineralogy, rock types, and space weathering. Current methods for these analyses tend to be computationally cumbersome, sensitive to noise and other factors, and poorly constrained with confidence limits. For problems of unmixing spectral signatures of mixtures of minerals, machine learning methods can yield a more accurate alternative to physical mixing models such as the Modified Gaussian Model. "Whole-spectrum matching" is a technique that enables large-scale analyses of spectra and avoids costly and error-prone peak-fitting and dimension reduction steps. It exploits all available data to compute similarity scores between pairs of spectra. In this presentation, we demonstrate the application of whole spectrum matching to infrared and Raman spectroscopy of minerals and their mixtures.These methods contrast with commonly used peak-fitting and dimension reduction techniques, which solve for a small number of explicit features before computing similarity. Instead, whole-spectrum methods preserve information by avoiding computation of features, making minimal assumptions about data structure and complexity. For example, a peak-fitting algorithm must by necessity threshold the number and quality of peaks reported, which may discard important information when applied to noisy data. Linear dimensionality reduction methods like principal component analysis also impose artificial constraints on data structure, and may become especially harmful in settings with small numbers of training samples.While we do not compute explicit feature representations, preprocessing remains a critical component of whole-spectrum matching algorithms. The entire preprocessing scheme may be broken into several steps of sequentially applied transformations, each of which is applied to all bands of all spectra. These transformation functions must generally satisfy a loose monotonicity requirement, ensuring that the sign of the first derivative of each spectrum will not change, while allowing for changes in the original signal and its higher order derivatives. In this way, relevant properties of spectra are captured without giving undue weight to noise. One unique feature of whole-spectrum analysis is the flexibility it provides regarding spectral data representation. Most existing methods require input in the form of a feature matrix, so all spectra must be resampled to fit a common, fixed-length, one-dimensional vector representation. Whole-spectrum methods eschew this requirement, however, allowing for a more natural "trajectory" representation in whicheach spectrum is stored as an ordered sequence of pairs, denoting the original wavenumber and intensity values. With this trajectory format, no constraints are imposed on the sampling rate or end points of each spectrum. This removes the necessity of resampling altogether, and allows efficient similarity computation for pairs of spectra with large non-overlapping regions. In addition, spectra in vector format usually have thousands of dimensions, which can pose a significant computational challenge. Under a trajectory representation, however, individual points are sparsely connected with only two dimensions per point, which enables computationally efficient matching algorithms.This work supported by the RISE SSERVI.

Author: ARON CORAOR

ORAL

Geochemistry/Petrology

Simulating surface materials: Preparation for the Exploration of Airless Bodies

The spectral data of samples and surfaces of the Moon, Near Earth Asteroids, Phobos, and Deimos will provide invaluable information of the geochemical state of these bodies, necessary for guiding human exploration and sample return. In keeping with the RIS4E goals, we have initiated experimental synthesis of minerals under simulated airless body conditions in order to optimize interpretation of remote sensing data sets and for investigation of the spectral effects of simulated space weathering. Initial efforts have been directed towards assessing the potential for using Fe in plagioclase to distinguish lunar feldspathic terrains, terrains that otherwise are characterized by limited variability in plagioclase composition. For lunar plagioclase, the Fe and Mg contents may rival the abundance of Na. We will report here the results of our efforts to synthesize anorthitic plagioclase with variable Fe contents. The synthesis experiments were designed to grow plagioclase that (i) is in equilibrium with a melt that would stabilize olivine at a lower temperature, but at higher temperature has only plagioclase on the liquidus, (ii) is in equilibrium with metallic Fe, and (iii) is from a melt in which early spinel stabilization has been avoided by the addition of some additional excess silica in the mix (which adds a pyroxene component to the melt). The synthesis experiments involved loading Fe capsules with a well-homogenized mixture of oxides, silicates, and Feo sponge + hematite (to make FeO), placing the capsules (with a constrictor ring to prevent escape of silicate melt) into silica glass tubes and then evacuating these tubes before loading them with enough N2 to provide about an atmosphere of pressure at the synthesis temperature. These tubes were placed in a platform furnace and heated above the liquidus, and cooled to a temperature that remained above the saturation temperature of mineral phases other than plagioclase. Characterization of the material requires consideration of the analytical challenges inherent to low Na compositions and the possibility of secondary Fe-fluorescence when droplets of metallic Fe are present in the plagioclase. Once these materials have been well characterized compositionally and used for Vis-NIR and mid-IR studies, these samples will be used for dust toxicity studies.

Author: M. DARBY DYAR

ORAL

Geochemistry/Petrology

Valence State Measurements of Minerals using X-ray Absorption Spectroscopy

The oxidation state of igneous materials on a planet reflects the degree of oxidation of the magma source region and in some cases the additional effects of magma interaction with the near surface environment and the solar wind. We are developing techniques for pico- and nano-scale interrogation of primitive planetary materials to determine valence state of multivalent elements including Fe, Ti, and V using synchrotron micro-XAS spectroscopy, which makes use of the pre-edge, main edge, and EXAFS regions of absorption edge spectra. Our current work focuses on creating calibration data and protocols for determining valence states in isotropic phases (glass, maskelynite) and anisotropic minerals including olivine, pyroxene, and feldspars. In the latter group of phases, the polarized X-ray beam interacts with each crystal differently as a function of orientation (X-ray pleochroism). Moreover, XAS spectra of geologic samples have been shown to be sensitive to both the abundance of the species in each valence state and the geometry of the coordination polyhedra surrounding them. Thus our calibrations must take into account all three variables that cause changes in the intensities of XAS features: optical orientation, valence state, and polyhedral distortion of each multivalent element site.The key to accurate predictions of valence state lies in the use of multivariate analysis techniques, which take advantage of valuable predictive information not only in the major spectral peaks/features, but in any channel of the entire XAS spectrum. Algorithms for multivariate analysis that "learn" the characteristics of a data set as a function of varying sample characteristics as orientation can then be applied to the spectrum of an unknown. We show here the impressive results of prediction models from one such technique, partial least-squares regression. The models and the resultant predictions improve with each addition of new spectral calibration data, overcoming drawbacks imposed by orientation effects, variable composition, and differences in crystal structures as long as there are adequate calibration standards.

SSERVI-ESF14-076

Author: KYEONG KIM

POSTER

Geochemistry/Petrology

ELEMENTAL ANALYSIS USING A PORTABLE X-RAY SPECTROMETER FOR PLANETARY SURFACE EXPLORATION APPLICATIONS

Active X-ray spectroscopy is commonly used to investigate the elemental composition of planetary surfaces. This technique could be used on a small rover (~20 kg), which is proposed for the prospective Korean lunar mission in 2020. As a first step toward an active X-ray spectrometer (AXS), we have conducted a preliminary scientific investigation using an X-ray spectrometer and an X-ray generator (XRG), which were commercially available from Amptek Inc., to carry out elemental analyses of standard samples and of various rock types. The XRG is a recently-developed technique, and uses a pyroelectric crystal with a broad 8 keV X-ray beam, producing 3*10^8 photons per second. We investigated the X-ray flux stability of the XRG, and it was found to be within +/-10%. This variance is likely caused by an increase in ambient temperature with time. The elemental analysis of four artificial samples using oxides of SiO_2, Al_2O_3, CaO, TiO_2, and Fe_2O_3 and one lunar simulant sample (FJS-1) confirmed a linear relationship between the elemental XRF count ratios and elemental abundance ratio. This result allows a good sample calibration and quantification of elemental abundance for prospective analysis of unknown samples. The elemental calibration curves of Ti/Fe and Ca/Fe ratios provided the elemental abundances of four representative unknown samples of volcanic rock, non-magnetic rock, feldspathic rocks, magnetic rock, and the elemental characteristics of these unknown samples lie on the calibration line. This permits the determination of the elemental ratios, which can be compared with the known elemental abundance information of standard samples. It was observed that finer grain sized samples provided a less scattered linear calibration curve than less uniform grain-sized samples. This study is aiming for both classification and quantification of various types of lunar analog rocks using the elemental analysis by the in-situ X-ray spectrometer, with application to planetary surface exploration conducted by a roving vehicle. This presentation introduces preliminary scientific results and recent technical development of our in-situ XRF analysis.

Author: ANTONIO LANZIROTTI

POSTER

Geochemistry/Petrology

Synchrotron-based microXAFS for probing the oxidation state of extraterrestrial igneous systems

For the vast majority of small extraterrestrial samples that would available from planned sample return missions, traditional macroscopic geochemical techniques are poorly suited. However, advanced synchrotron-based techniques such as microXAFS can be useful to characterize the geochemistry of such small samples, particularly for probing the oxidation state of igneous materials. These measurements can be used to evaluate the degree of oxidation of a planetary magma source region and, possibly, the additional effects of magma interaction with the near surface environment. Synchrotron microXAFS can help constrain the intrinsic oxygen fugacity (fO2) of magma as a direct measure of its oxidation state. We are continuing to develop techniques for pico- and nano-scale interrogation of primitive planetary materials for determining elemental valence state as a proxy for fO2. Multivalent element buffers offer the opportunity to develop oxybarometers based on valence state proxies that span the entire oxygen fugacity range of Solar System evolution. Examples of the systems we are continuing to develop in cosmochemistry include: (1) at the oxidized end of the scale represented by Earth, the Fe valence oxybarometer of terrestrial igneous systems, (2) for Mars under somewhat more reduced conditions, Eu valence oxidation state measurements and (3) under the highly reducing conditions experienced by refractory inclusions (solar gas ~ IW-7), Ti valance state analysis. We have also been developing methodologies for using V valence, species that cover a broad range between oxidizing and reducing conditions. Examples will be discussed.

Author: ANTONIO LANZIROTTI

POSTER

Geochemistry/Petrology

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SSERVI-ESF14-079

Author: MAURIZIO PAJOLA

ORAL

Geochemistry/Petrology

Is Phobos capture origin a priori excluded from its low bulk density?

Flybys of Mars Express confirm the low density of Phobos with the derived value of 1.876 ± 0.02 g/cm3 (Andert et al., 2010, Witasse et al., 2013, Paetzold et al., 2013). Such a value strongly argues in favour of a Phobos formation from a disk of debris (Peale 2007) whether as a remnant of the formation of Mars (Safronov et al., 1986) or as the result of a collision between Mars and a large body (Craddock 1994, 2011; Singer 2007). Within this scenario a low density of the re-accreted material forming Phobos is expected, due to large interior porosity. Thermal emission spectra of Phobos suggest an ultramafic composition with the presence of phyllosilicates and feldspathoids in some regions (Giuranna et al., 2011). Such data would be consistent with formation of Phobos near its current location (1.4-1.7 AU) or in situ (Giuranna et al., 2011).The difficulties in understanding the origin of Phobos arises from the fact that the 0.3-4.0 _m surface spectra taken from multiple areas of the body in more than 43 years of observations (Duxbury et al., 2013), show physical characteristics similar to low-albedo asteroids such as C-type (Masursky et al., 1972, Pang et al., 1980) or D-type (Murchie 1999, Rivkin et al., 2002, Lynch et al., 2007, Pajola et al., 2012). These data argue against an in-situ formation leading to an asteroidal capture scenario: this can be favoured by binary asteroid dissociation (Landis 2009) or by collisional capture in the Martian orbital region (Pajola et al., 2012). Recent data (Schmedemann et al., 2014) suggest an ancient surface age for Phobos of ~ 4.3 – 3.7 Ga, dating back to a period where there was an intensification in the number of impactors in the inner Solar System (Gomes et al., 2005), supporting both the in-situ and the captured scenario. Pajola et al. (2013) presented a mineralogical model composed of a mixture of Tagish Lake meteorite (TL) and Pyroxene Glass (PM80) to explain the surface reflectance of Phobos from 0.4 to 4.0 _m. Starting from the reasonable fit between the proposed model and Phobos spectra, we adopted the weighted TL and PM80 densities to investigate if low bulk density of Phobos could be matched by these components reconciling both inner properties and surface spectra. TL density is available from measurements by Hildebrand et al. (2006), but the density of PM80 (Jager et al., 1994) has not been measured. In order to overcome the lack of density data for the above mentioned pyroxene glass, we have considered density values of different pyroxene glasses from the literature (Karamanov and Pelino, 1999, and Smithsonian Physical Tables 1921) and the density of mafic-rich glasses with VNIR spectra similar to PM80 (Carli et al., 2014). The obtained results will be presented.

Author: PATRICK PEPLOWSKI

ORAL

Geochemistry/Petrology

Abundances of H and major-elements on asteroid 433 Eros: Revisiting the in-situ measurements of the NEAR Gamma-Ray Spectrometer

We have reanalyzed gamma-ray measurements taken on the surface of asteroid 433 Eros by the Near-Earth Asteroid Rendezvous (NEAR) spacecraft. This dataset represents the first in-situ measurements acquired from the surface of an asteroid, and it provides important insights into the composition of near-earth asteroids. Our reanalysis, which utilizes improved knowledge of the detector response and gamma-ray production physics, has allowed us to link the composition of Eros to the LL-chondrites. Additionally, comparisons of Fe gamma rays from neutron inelastic scatter and neutron capture reactions provide constrains on the hydrogen content of the regolith. Our H abundance value of 0 to 300 ppm represents the first in-situ measurement of the hydrogen content of an asteroid. This value is lower than the average H content for LL-chondrite meteorites, both finds and observed falls, and suggests that hydrogen may be depleted in near-surface materials on Eros. This is consistent with observations of the depletion of the moderately volatile element S by the NEAR X-Ray Spectrometer. Depletion of volatile elements on asteroids has implications for human exploration and resource utilization of near-earth asteroids.

Author: SARA PORT
POSTER

Geochemistry/Petrology

Quantifying hydroxyl radical production from pulverized olivine with Electron Spin Resonance (ESR) spectroscopy

Recent research has demonstrated that when several different types of minerals, such as olivine, augite, and quartz, are pulverised in the laboratory, reactive oxygen species, or "ROS", are produced, including hydrogen peroxide, superoxide, and hydroxyl radicals. These reactive compounds can be hazardous to humans, as they are highly reactive with organic matter. This makes ROS production an important phenomenon to study in an effort to assess the potential health impacts to astronauts sent to other planetary bodies within our solar system, where fine-grained, pulverized mineral dusts are found in abundance. These mineral dusts are thought to be produced by meteorite impacts into planetary surfaces as well as mechanical weathering by aeolian processes on dry planets with atmospheres, such as Mars. It is relatively unknown how much of these reactive compounds are produced, or how much pulverization is required in order to yield a measurable amount of ROS. In order to determine this, we are performing research on pulverized olivine, an abundant mineral on basaltic planetary bodies such as the Moon, Mars, and asteroids, and which is known to produce reactive hydroxyl radicals.In order to accurately quantify hydroxyl radical production, we use ESR spectroscopic measurements of the stable free radical compound Tempol (4-hydroxy-2, 2, 6, 6-tetramethylpiperidin) to generate linear calibration curves that permit quantification of radical concentrations as low as 1 micromolar. For our experiments, we grind olivine using a planetary ball mill with an agate grinding bowl and agate grinding balls. We then expose the ground olivine to a dilute solution of the spin trapping compound 5, 5-Dimethyl-1-Pyrroline-N-Oxide, or DMPO. OH radical is produced as a by-product of reactions between pulverized olivine and water, but because OH radical is highly unstable, it is necessary to use DMPO to "trap" or stabilize the radical as a DMPO OH-radical adduct for measurement by ESR. The slurry of DMPO, water, and olivine are allowed to react for a prescribed period of time while being agitated, and the slurries are then centrifuged to separate the solids and liquids. The supernatant is then measured by ESR and can be quantified using a Tempol calibration curve.Our initial measurements have verified that OH-radical is indeed produced by pulverized olivine, and furthermore, that the combination of ESR spectroscopy, Tempol calibration, and DMPO spin trapping should produce robust, quantitative measurements of mineral reactivity. We will report on our quantitative assessment of olivine reactivity, and our ongoing work will explore the reactivity of olivine and other relevant mineral phases in effort to protect future explorers visiting planetary surfaces in the Solar System.

Author: MELINDA RUCKS

POSTER

Geochemistry/Petrology

MID IR Optical Constants of Orthopyroxenes

Orthopyroxenes are common rock forming minerals that are present on many planetary bodies as well as meteorites and cosmic dust. The presence of these minerals can give implications to the petrogenic history of these planetary bodies. Optical constants, n and k, are essential inputs into radiative transfer models which are used in remote sensing techniques. [1,2] While optical constants have been determined for orthopyroxenes with high Mg content, Fe rich orthopyroxenes have not been studied as extensively. [3] The goal of this research is to determine the optical constants of orthopyroxenes ranging in composition along the enstatite-ferrosilite solid solution, to gain a more comprehensive list of these values. Specular reflectance spectra, in the range of 250-4000 cm-1, were obtained for several oriented single crystal samples at three crystallographic orientations for each sample. Optical constants, n and k, were then derived through modeling of measured spectra using the Matlab lsqcurvefit function. Preliminary research on natural Mg rich orthopyroxene samples has shown comparable results to previous studies. Future work will apply this method to orthopyroxene samples with higher iron content.[1] Arnold, J.A. et al (2013) (under review), [2] Glotch, T.D. and Rossman, G.R. (2009) Icarus, [3] Jäger, C. et al (1998) Astron. Astrophys.

SSERVI-ESF14-083

Author: MARTIN SCHOONEN

ORAL

Geochemistry/Petrology

Reactive Oxygen Species Generation by Lunar Simulants

With the eventual deployment of human explorers to near-Earth, airless planetary bodies and the establishment of a long-term manned research site on the Moon or other Target Bodies, it is inevitable that humans will be exposed to local mineral dust. Repetitive inhalation exposure to mineral dust in industrial settings is considered an occupational health risk, which can lead to various lung ailments. While daily and lifetime exposures for human explorers are expected to be far less than for those working a lifetime in industrial settings, the mineral dust that human explorers will likely be exposed to is expected to be highly reactive due to the presence of unsatisfied surface bonds and nanophase metallic iron. Mineral inhalation exposure can lead to inflammation, cytotoxicity (i.e., toxicity to cells), genotoxicity (i.e, damage to DNA), and fibrosis. One of the factors possibly contributing to the toxicity of a material is its ability to generate Reactive Oxygen Species (ROS). ROS are oxygen-containing species are chemically reactive molecules containing molecular oxygen. In vitro, the step-wise reduction of molecular oxygen leads to the formation of superoxide radical (O2*-), hydrogen peroxide (H2O2) and hydroxyl radical (OH*). Hydroxyl radical is by far the most damaging to biomolecules. In vivo, the immune system triggers the formation H2O2 when challenged with a foreign substance. Cellularly-derived H2O2 can react with transition metal-containing minerals to generate OH* via the Fenton reaction. In this contribution, we report results of an ongoing study to determine the spontaneous generation of OH* upon dispersion of lunar simulants in water as well as through conversion of H2O2. The OH* formation was quantified using both Electron Spin Resonance (ESR) spectroscopy and molecular probes. ESR combined with spin trapping using 5,5-Dimethyl-1-pyrroline N-oxide (DMPO) provides an assessment of the initial formation of OH*, while the molecular probe provides insights into the formation of OH* over periods up to 12 days. A suite of lunar simulants, including JSC-1A and NU-LHT-2M , were investigated. We have evaluated the spontaneous formation of OH* as a function of mechanical stress by hand grinding as well as the formation of OH* through the interaction between H2O2 and simulant. We also plan to evaluate the effects of UV irradiation and dehydroxylation on these simulants as well as to determine the formation of OH radicals upon the dispersion of treated and untreated simulants in simulated lung fluid. ESR spin trap results thus far indicate a modest increase in the amount of OH* released as a result of mechanical stress. This is likely associated with the formation of broken bonds at mineral surfaces. Additional studies are needed to determine if this treatment imparts reactivity that lasts for more than a few minutes. Experiments with untreated simulants and H2O2 using a molecular probe showed no formation of OH* within 286 hours.